

Ferrodistortive instability at the (001) surface of half-metallic manganites

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We present the structure of the fully relaxed (001) surface of the half-metallic manganite $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, calculated using density functional theory within the generalized gradient approximation (GGA). Two relevant ferroelastic order parameters are identified and characterized: The tilting of the oxygen octahedra, which is present in the bulk phase, oscillates and decreases towards the surface, and an additional ferrodistortive Mn off-centering, triggered by the surface, decays monotonically into the bulk. The narrow d -like energy band that is characteristic of unrelaxed manganite surfaces is shifted down in energy by these structural distortions, retaining its uppermost layer localization. The magnitude of the zero-temperature magnetization is unchanged from its bulk value, but the effective spin-spin interactions are reduced at the surface.

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A good understanding of the surface physical properties in colossal magneto-resistant hole-doped manganese oxides is highly desirable for future applications of these promising materials in magnetoresistive devices or spintronics. [1] The metallic phase of $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{A} = \text{Sr}, \text{Ca}$), obtained for $x \sim 0.3$ is of particular interest because of its high spin polarization at the Fermi level. There is some controversy, however, on whether this optimally doped phase is a half-metal, with a gap for one spin direction, and thus with fully spin-polarized carriers. Early spin-resolved photoemission experiments observed such ideal polarization [2], although electron tunneling experiments show traces of partial occupation of minority spin states [3]. Since these techniques probe the bulk structure through the surface or interface, (as do most techniques for bulk studies with variable degrees of surface sensitivity), the origin of these discrepancies could lie not only in the difficulty in preparing smooth surfaces at an atomic level, but also in the fact that the properties of the surface may markedly deviate from those of the bulk. The primary goal of this work is to determine the structural changes induced by surface termination at the (001) surface of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO). In addition, we discuss the influence of these structural changes on the electronic properties.

The theoretical description of the half-metallic manganites is challenging given the strong correlations of the transition metal d electrons, as well as the complex chemistry and large range of possible structural distortions from the high symmetry perovskite structure. For example, *ab initio* studies based on the local spin density approximation (LSDA) give poor agreement with the experimental lattice constant; as a result many first principles calculations to date have been performed for cu-

bic structures with the experimental pseudocubic lattice constant and without structural relaxations. However, the strong electron-lattice interactions are known to play an important role in the electronic properties, and a full description of the lattice distortions, particularly at surfaces or interfaces where local distortions might be more pronounced, is desirable. Furthermore, LSDA fails to obtain a half-metallic state for $x = 0.3$ [4], and it has been argued that a more accurate treatment of electron correlation, such as LSDA+ U or self-interaction corrected (SIC) is required, particularly for the charge-ordered or insulating phases [5, 6].

Here we present *ab initio* results for a fully relaxed LSMO (001) surface obtained using density-functional theory within the generalized gradient approximation (GGA). Our choice of exchange-correlation functional was motivated by our recent GGA calculations for bulk $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO), [7] in which we found good agreement between the theoretically optimized pseudocubic and experimental lattice constants, and qualitatively correct half-metallic electronic behavior. Since our focus is on structural, rather than on electronic properties, and since we are interested in the metallic phase of LSMO, which reduces the errors related to the non-locality of the exchange-correlation hole, we elect not to include higher order descriptions of correlation effects such as in the GGA+ U method. Indeed, it was recently shown [8] that the use of GGA+ U does not significantly change the structural properties. However the limitations of today's GGAs for treating highly-correlated systems should be kept in mind, in particular when we discuss changes in the surface electronic spectral properties based on Kohn-Sham eigenvalues [9].

Our calculations were performed using the SIESTA im-

plementation of density functional theory [10, 11]. Core electrons were replaced by norm-conserving pseudopotentials [12], and finite-support numerical atomic orbitals were used to describe the valence electrons, at the double- ζ polarized level [13]. Semicore states for Ti ($3s^2$ and $3p^6$), Sr ($4s^2$ and $4p^6$), and La ($5s^2$ and $5p^6$) were included in the valence. The spin-polarized gradient-based PBE exchange-correlation functional was used [14], with a grid cutoff of 320 Ry for integrations in real space. Atomic positions were relaxed until the forces were smaller than 25 meV/Å.

To validate our method in obtaining relaxed atomic structures, we first studied the properties of bulk LSMO. We built a cell that is a $\sqrt{2} \times \sqrt{2} \times 2$ repetition of the ideal perovskite cubic cell, and performed a variable cell relaxation of the crystal structure. Our calculated lattice parameters are within 2 % of the experimentally reported values, and our Mn-O bond lengths (1.96 Å) are even closer to experiment (1.95 Å) [15]. The tilt angle (6.6°) that we obtain for the optimized structure is in excellent agreement with the experimental value (6.8° [15]). Since these distortions are believed to be the source of the strong electron-phonon coupling in manganites [16] (they lift the degeneracy of e_g levels, as recently shown in photoemission experiments [17], and reduce the electronic energy for single occupancy of this state) their accurate representation in our calculations is essential.

To study the surface, we consider a supercell structure with 4×2 repetitions of the original cubic cell in the surface *ab*-plane, eleven atomic layers (5.5 unit cells) along the direction perpendicular to the surface, and MnO_2 termination at both sides of the slab [18]. We begin with a pseudocubic structure and allow for atomic relaxations, while keeping the in-plane lattice parameters fixed to the relaxed bulk values. The supercell is large enough to accommodate the octahedral tiltings, and commensurate with the orthorhombic phase in the *ab* plane. The surface breaks the bulk rhombohedral symmetry, most importantly the three-fold axes of the $R\bar{3}c$ phase, therefore falling back onto the *Pnma* tilt system. Doping is then introduced explicitly by substituting La atoms by Sr, with the resulting structure having a quasi-random distribution of 13 Sr atoms and 27 La atoms. The system is thick enough to ensure that the electronic structure at the center of the slab is similar to that of the bulk.

We find that relaxation of the atomic positions gives rise to a buckling in the surface layer, with the Mn atoms shifted out of the plane. There is also a change in the octahedral tiltings and of the Mn-O bonding distances. In Fig. 1(a) we plot the tilting angle of the MnO_6 octahedra as a function of the position of the Mn layer across the slab. It can be seen that in the central layers, the tilting approaches the value obtained for the relaxed bulk structure (dashed line) while it reduces towards the surface. In addition, we find that the buckling of the Mn atoms with respect to oxygens in the surface layer propagates

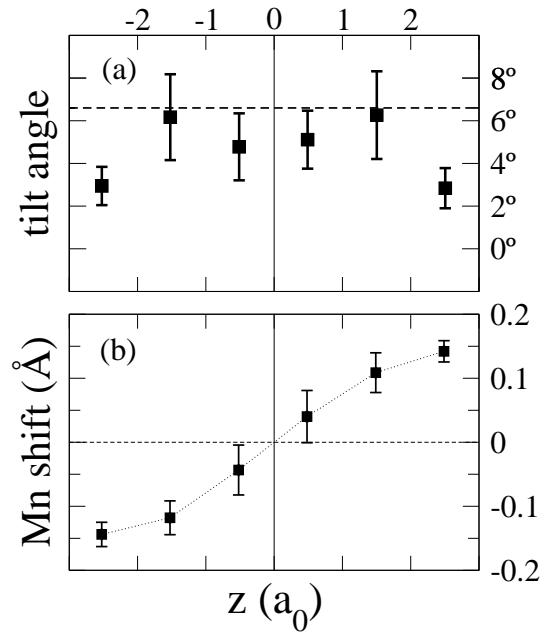


FIG. 1: (a) Octahedral tilt angle versus position across the slab, z , in units of the cubic lattice constant, a_0 . The dashed line shows the value for the theoretically relaxed bulk geometry. (b) Off-centering (in Å) of the Mn atoms from the plane defined by the neighbouring O atoms in the MnO_2 layer. The z origin is defined at the center of the slab. Error bars indicate the differences within the same atomic layer.

to the subsurface giving rise to an off-centering similar to that of ferroelectric perovskites. The magnitude of this off-centering, shown in Fig. 1(b), decays monotonically towards the center of the slab, where it is zero due to the cancelling effect of both surfaces. The distortion results in important changes in the Mn-O bonding distances along the z direction, whereas the in-plane bonds remain essentially unchanged.

Although the Mn-O buckling at the surface layer is a result of local surface chemistry (see the surface-state shift below), the off-centering deeper into the bulk is not. The situation is better described as a polar, ferroelastic instability, which is triggered by the surface buckling. Since this instability is not dominant in the bulk phase, it therefore decays from the surface into the bulk. Such surface-triggered decaying ferroelastic distortions are described in the literature [19], and can be very slowly decaying [20]. Our calculations, however, allow us to ascertain only that the decay length λ_o is not smaller than $\sim 10\text{\AA}$, since the antisymmetric character of the order parameter [Fig. 1(b)] forces it to go through zero at the center of the slab.

The length-scale of the decay towards the surface of the octahedral tilt order parameter, λ_t , should be captured in our calculations, since the symmetry of the slab does not constrain it in this case. We find that it is of the or-

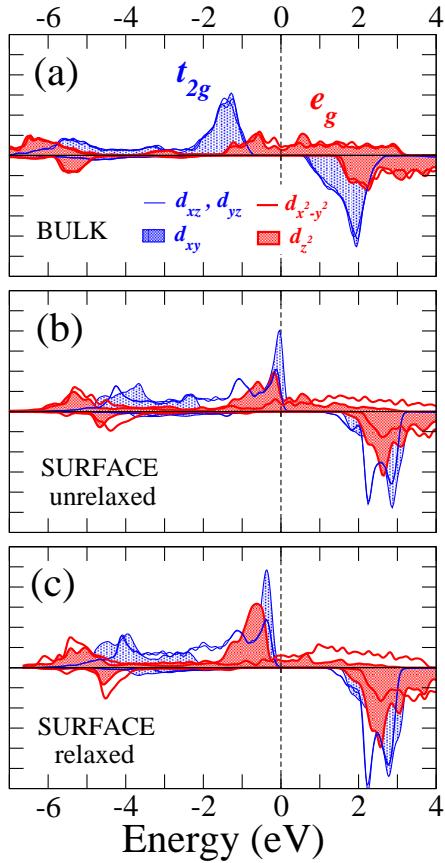


FIG. 2: (Color online): Partial density of states for up/down spins (top/bottom) for the Mn 3d orbitals in the center of the slab (a), and the surface layer before (b) and after (c) the structural relaxation. The surface state is mainly composed of d_{z^2} and d_{xy} orbitals, which are shown as shaded regions.

der of a few atomic layers. However, we can not rule out the possibility that both order parameters are coupled at the surface, whereby λ_t would be in fact determined by the constraint on λ_o . Indeed, couplings and/or competitions between polar ferroelectric modes and tiltings and rotations of oxygen octahedra are well known to occur in related perovskites [21, 22, 23]. Interestingly, however, the decay of the untilting seems oscillatory and commensurate with the crystal; both monotonic and oscillatory behaviors can be expected in surface ferroelastic decays [19].

Although not the main focus of this work, next we briefly compare the bulk and surface electronic structures within the GGA. Fig. 2 shows our calculated Mn 3d partial densities of states (PDOS) in the center of the slab (a), and for unrelaxed (b) and relaxed (c) surface configurations. At the center of the slab, the system is half-metallic, with e_g character for the states at ε_F , and localized t_{2g}^\uparrow states around 1.5 eV below, in fair agreement with previous calculations [4] and photoemission experiments [24]. Importantly, this half-metallicity per-

sists at the surface, and since the majority spin metallicity results from a broad Mn 3d - O 2p hybridized band (the Mn d_{z^2} and $d_{x^2-y^2}$ states, as well as the p_z of the oxygen underneath the Mn, dominate the Fermi level at the surface) it is likely to be accurately represented in our GGA methodology. For the unrelaxed (cubic) structure, the surface termination induces a localized surface state, of mainly d_{z^2} and d_{xy} character. This state had been previously observed in LSDA and SIC-LSDA calculations with unrelaxed cubic surface geometries, and originates after the splitting of the states $e_g \rightarrow d_{z^2}, d_{x^2-y^2}$ and $t_{2g} \rightarrow d_{xy}, (d_{yz}, d_{xz})$ related to the surface-induced symmetry breaking, from cubic O_h to C_{4v} [25, 26]. The surface state shifts to lower energies away from ε_F when the geometry relaxes. This is the driving force for the surface buckling.

Concerning magnetic properties, we observe that the zero kelvin magnetic moment remains almost unaltered up to the very surface, with a value of $3.55\mu_B$ at the relaxed surface compared with $3.53\mu_B$ in the bulk. The ground state remains ferromagnetic. In order to address the finite temperature magnetism, we explored different magnetic configurations and found that the energetic cost of reversing one magnetic moment at the surface is reduced to 30% of the bulk value, indicative of lower effective magnetic interactions, and in line with experimental results [2]. Forces on the atoms of up to $1.54 \text{ eV}/\text{\AA}$ ($1.01 \text{ eV}/\text{\AA}$) have been found upon single spin reversal in the surface (in the bulk), indicating (i) that the surface ferromagnetic coupling would weaken even more as compared to the bulk, and (ii) a possible important magnon-phonon coupling.

Two competing considerations arise when relating the magnetic results to the structural ones. The double-exchange (DEX) mechanism, in which localized 3d t_{2g} electron spins interact ferromagnetically through the e_g conduction-electron hopping between nearest neighbours, is frequently used to describe the electronic properties of manganites. On one hand, the electron-hopping energy among Mn e_g states in this DEX model is expected to decrease with the bending of the Mn-O-Mn bonds, in agreement with the observed reduction of the ferromagnetic Curie temperature T_M in doped manganites [27]. The octahedral untilting towards the surface discussed before would thus suggest a surface enhancement of hopping and T_M , at odds with the mentioned observations. On the other hand, however, the hopping energy should be much more affected by the substantial off-centering, thus altering the inter-layer coupling.

The surface-triggered ferrodistortive instability discussed above is very similar in kind and magnitude to that of ferroelectrics like BaTiO₃. It is thus tempting to consider multiferroic possibilities for this system. Considering the calculated values for the atomic displacements, and taking $\sim +3e$ for the nominal charge of Mn, we would obtain a polarization of $\sim 10\mu\text{C}/\text{cm}^2$ at the sur-

face layer, comparable to the values obtained in similar Mn-based multiferroics. It must be remembered, however, that it is a metallic system, and thus any polarization will be screened by the itinerant carriers. In addition to the ferroelastic characteristics discussed above, the surface buckling could display surface piezoelectric signatures, considering the Thomas-Fermi screening length of this (poor) metal, affecting the work function and its strain dependence. This could be a relevant consideration for understanding the orientation of dipolar molecules deposited on the surface. Spin valve devices based in LSMO have already been demonstrated with Alq3 (8-hydroxy-quinoline aluminum) [28], and a substantial shift in its molecular energy levels has been measured [29]. The LSMO surface dipole would favor the orientation of the Alq3 molecular dipole towards the vacuum side, and the resulting electrostatic potential would lower the molecular levels as observed [29].

It should be remembered that the presented results here are for the defect-free MnO_2 -terminated LSMO surface. They may be very different for (La,Sr)O termination [26], and, most importantly, in the presence of defects like oxygen vacancies. Recent photoemission experiments have suggested the presence of strongly localized Mn^{+2} states at the surface of LSMO, related to oxygen vacancies [30]. DFT results on the effect of these defects in this LSMO surface will be discussed elsewhere [31].

In conclusion, our first-principles structural relaxation of the LSMO (001) surface has revealed a surprising surface-triggered ferroelastic instability of an off-centering ferrodistortive kind. The distortion is driven by the surface electronic structure, and causes a weakening of the tendency to magnetic order close to the surface. We hope that our observations will stimulate further work towards the characterization of the discussed instabilities, as well as possible exploitation of the newly observed surface polarization and its coupling to the magnetic behavior.

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